(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 206 418 B1**

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **13.11.91** (51) Int. Cl.5: **C11D 3/386**, C11D 3/39

(21) Application number: **86201055.0**

(22) Date of filing: **18.06.86**

(54) Dry bleach and stable enzyme granular composition.

(30) Priority: **28.06.85 US 750569**

(43) Date of publication of application:
30.12.86 Bulletin 86/52

(45) Publication of the grant of the patent:
13.11.91 Bulletin 91/46

(84) Designated Contracting States:
BE DE FR GB IT LU NL

(56) References cited:
EP-A- 0 135 227
FR-A- 2 357 301
NL-A- 7 000 742
US-A- 4 421 664

(73) Proprietor: **THE PROCTER & GAMBLE COMPANY**
One Procter & Gamble Plaza
Cincinnati Ohio 45202(US)

(72) Inventor: **Herdeman, Robert William**
179 Dogwood Drive
Loveland Ohio 45140(US)

(74) Representative: **Ernst, Hubert et al**
PROCTER & GAMBLE EUROPEAN TECHNICAL CENTER N.V. Temselaan 100
B-1853 Strombeek-Bever(BE)

EP 0 206 418 B1

Description

BACKGROUND OF THE INVENTION

This invention relates to an improved dry bleach and stable enzyme granular compositions.

During the last score of years the use of enzymes, especially of microbial origin, has been more and more common. Enzymes are used in, for example, the starch industry to produce glucose and fructose by means of amylases, amylglucosidases and glucose isomerases. In the dairy industry a vast tonnage of rennets is used and in the detergent industry proteases are normally used as additives in the washing powders to impart a better action on proteinaceous stains on the laundry.

On July 7, 1970, C. B. McCarty was granted U.S. Pat. No. 3,519,570 for enzyme-containing detergent compositions and a process for conglutination of enzymes and detergents. U.S. Pat. No. 3,784,476, van Kampen et al., issued Jan. 8, 1974, discloses a particulate enzyme-containing detergent composition containing a detergent surface-active agent, a water-soluble builder salt and discrete, shaped inorganic solids containing proteolytic or amylolytic enzymes. It should be noted that this patent does not teach an enzyme granulate with alkaline buffer salt as defined herein (pH of 7-11) used in combination with a peroxyacid bleach as disclosed herein.

U.S. Pat. No. 4,106,991, Markensen et al., issued Aug. 15, 1978, discloses an improved formation for enzyme granulates comprising enzyme, inorganic salts, a granulation binder, and finely divided cellulose fibers as 2-40% by weight of the granulate. Optionally, a waxy substance can be employed for the granulating agent, or to coat the granulate.

The granulates so produced are reported by Markensen et al. to have a higher physical stability and a higher resistance against abrasion than granulates without cellulose fibers and, consequently, a very low dust level. Markensen et al. does not disclose that use of alkaline buffer salts would improve the enzyme stability in the presence of peroxyacid bleach.

After the development of the granulated and coated enzymes presently offered to the detergent industry, the use of the enzymes in detergents has grown steadily.

Making a storage stable mixture of enzyme containing granulates and dry peroxyacid bleach granulates is a difficult task. In spite of the fact that some commercially available enzyme granulates are advertised as "perborate bleach stable," they are weak storagewise in the presence of strong peroxyacid bleach granulates. It should be noted that peroxyacid bleach granulates are relatively newcomers to the dry commercial laundry detergent and bleach markets. The term "bleach" as used herein unless otherwise specified means peroxyacid bleach and the terms "peroxyacid bleach powder" and "peroxyacid bleach granulates" are synonymous unless otherwise specified. The term "enzyme" as used hereinafter means raw enzyme, unless otherwise specified. The term "enzyme powder" means a mixture of raw enzyme and inorganic salts.

SUMMARY OF THE INVENTION

This invention relates to an improved dry bleach and stable enzyme granular composition. The enzyme granulate comprises a homogeneous mixture of enzyme and alkaline buffer salt. The improved enzyme granulate is stable when mixed with peroxyacid bleach granulates.

OBJECTS

It is an object of the present invention to provide a dry bleach and stable enzyme granular composition. Other objects will become apparent in the light of this disclosure.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to an improved dry bleach and stable enzyme granular composition. The enzyme granulate comprises a homogeneous mixture of enzyme and alkaline buffer salt. The improved enzyme granulate is stable when mixed with peroxyacid bleach granulates. The term "granular" as used herein means the composition comprising: (1) enzyme granulates and (2) peroxyacid bleach granulates, unless otherwise specified.

This invention has an improved water-soluble enzyme granulate containing enzymes, fillers and/or binders and an effective amount of alkaline buffer salt to protect the enzyme from de-activation via contact with peroxyacid bleach granulate. The alkaline buffer salt has a pH of from 7 to 11. The level of alkali buffer

salt material contained in the granulate is from 3% to 97.5% by weight of the enzyme granulate. An alkaline buffer salt material as used herein is defined as a material having an effective amount of alkaline buffer salt and compatible inorganic salts. The used ratios of raw enzyme to alkaline buffer salt material are from 1:4 to 1:200, preferably 1:6 to 1:100, and more preferably 1:20 to 1:50.

The improved enzyme granulate on a weight percentage basis preferably comprises:

TABLE 1

Enzyme Granulate Levels (%)

Ingredient	Preferred	Low	High
Proteolytic Enzyme	4	0.5	15
Amylase Enzyme	1	0	5
Alkaline Buffer Salt Material	45	3.0	97.5
Cellulose Filler & Binder	25	2.0	40
Optional Waxy Coating	25	0	57

The weight percentages used herein refer to the weight of the granulate being discussed, unless otherwise specified.

The improved enzyme granulate is made with a raw enzyme level of from 0.5% to 20% (0.25 to 10 Au/gram), and preferably from 1% to 10% (0.5 to 5 Au/gram) by weight of the total composition. Au equals Anson units and is a term commonly used in the trade to describe enzyme activity. The cellulosic filler and binder in the enzyme granulate have a ratio of from 1:1 to 10:1. The level of cellulosic fillers in the total composition is from 2% to 40%, preferably from 2% to 36%.

The stability of the alkaline buffer salt material/enzyme granulate of this invention is further improved with the inclusion of an antioxidant salt to the granulate. The antioxidant is preferably used at a level of from 1% to 40%, more preferably 2% to 30%. The enzyme granulate of this invention is further improved if it has a coating of alkaline buffer salt material including antioxidant with an overcoat of water-soluble nonionic waxy material over said coating. A coating level of at least 10% alkaline buffer salt material by weight of the enzyme granulate is preferred. The waxy overcoat is preferably used at a level of 10% to 30% and more preferably 15% to 25% by weight of said granulate.

Granular Compositions

The improved granular composition of this invention is a mixture of peroxyacid bleach granulates, improved enzyme granulates and, optionally, other laundry active powders including softeners and detergents having a weight ratio of from 1:1 to 1:1500 of enzyme granulate to bleach granulate. Examples of powdered detergent materials are disclosed in U.S. Pat. No. 4,404,128, B. J. Anderson, issued Sept. 13, 1983. Examples of detergent composition and builder salts are disclosed in U.S. Pat. No. 3,784,476, van Kampen et al., issued Jan. 8, 1974. Examples of powdered peroxyacid bleach granulates are disclosed in U.S. Pat. No. 4,473,507, F. P. Bossu, issued Sept. 25, 1984. Suitable granular compositions can be formulated within the following ranges:

TABLE 2

Ingredient	Weight %
Bleach granulate	0.5-98
Enzyme Granulate	0.1-15
Brightener	0-3
Alkali metal builder salts*	0-80
Anionic surfactant	2-30
Nonionic surfactant	1-10
Ammonium and sodium sulfate	0-80
Perfume	0-1
Other laundry ingredients/ additives, i.e., softeners	0-20

*Orthophosphates, pyrophosphates, tripolyphosphates, nitrilotriacetates, ethylenediamine tetraacetates, carbonates and silicates.

A preferred mixture is an enzyme-peroxyacid bleach granular composition comprising the alkaline buffer salt protected enzyme granulate of this invention and a peroxyacid bleach granulate having a weight ratio of from 1:1 to 1:1500 of enzyme granulate to bleach granulate, preferably 1:3 to 1:30. Details of such a preferred mixture is disclosed below.

The Alkaline Buffer Salt Material

The term "alkaline buffer salt material" as used herein means a salt having a pH of 7-11 and which provides a comparable pH for the enzyme granulate in the presence of acidic substances for an extended period of time. Thus, the alkaline buffer salt material useful in the present invention can include any one of a number of suitable compatible inorganic salts which have a pH of 7-11. A pH of 8-10 is preferred. The pH of a salt is measured as a 10% solution of the salt. Some preferred alkaline buffer salts are potassium bicarbonate, potassium carbonate, tetrapotassium pyrophosphate, potassium tripolyphosphate, sodium bicarbonate and sodium carbonate. Other suitable alkaline buffer salts can be used.

The alkaline buffer salt material can constitute 97.5% of the solids in the enzyme granulate. In this case at least 2% is cellulosic fibers and 0.5% enzyme per Table 1. However, other compatible materials can be included as part of the alkaline buffer salt material, e.g., other inorganic salts, fillers and binders. Calcium is a preferred component and can be added as calcium sulfate or calcium chloride.

The Antioxidant

As used herein the term "antioxidant" means a substance that opposes oxidation or inhibits reaction provided by oxygen or peroxides. The antioxidant is an enzyme stability booster for the alkaline buffer salt enzyme granulate. The antioxidant increases the stability of the enzyme when used in conjunction with alkaline buffer salt. The preferred enzyme granulate can contain an antioxidant salt, preferably at a level of from 1-40%, and more preferably 2-30% by weight of the enzyme granulate. Some preferred antioxidant salts are sodium sulfite, sodium bisulfite and sodium thiosulfate. Other suitable antioxidant salts can be used.

The Enzyme Granulate

The enzyme granulate of the present invention has preferably a particle size of from 100 to 1600 micrometers, more preferably from 200 to 800 micrometers, most preferably 300-500 micrometers.

A preferred process for making enzyme granulates of this invention comprises drum granulating an enzyme material, inorganic salts, a granulation binder, a liquid phase granulating agent, and finely divided cellulose fibers. In accordance with the present invention the inorganic salts are selected to include an effective amount of alkaline buffer salt material to protect the enzyme from rapid deactivation upon exposure to peroxyacid bleach granulates.

The process for the production of enzyme granulates comprises e.g., the introduction into a drum granulator of from 2 to 40% by weight of cellulose in fibrous form, from 0 to 10% by weight of a binder as herein defined, 0.5% to 20% enzyme and 3% to 97.5% alkaline buffer salt material in an amount which generates the intended enzyme activity in the finished granulate, a liquid phase granulating agent consisting of a waxy substance, as defined herein, and/or water, in an amount of between 5 and 70% by weight, whereby the maximum amount of waxy substance is 40% by weight and the maximum amount of water is 70% by weight, whereby all percentages are referring to the total amount of dry substances, the sequence of the introduction of the different materials being arbitrary, except that at least a major part of the granulating agent is introduced after at least a substantial part of the dry substances is introduced in the granulator, whereafter the granulate, if necessary, is dried in a conventional manner, preferably in a fluid bed.

The cellulose in fibrous form can be sawdust, pure, fibrous cellulose, cotton, or other forms of pure or impure fibrous cellulose. Several brands of cellulose in fibrous form are on the market, e.g., CEPO and ARBOCEL. In a publication from Svenska Tramjolsfabrikerna AB, "Cepo Cellulose Powder," it is stated that for Cepo S/20 cellulose the approximate minimum fiber length is 500 micrometers, the approximate average fiber length is 160 micrometers, the approximate maximum fiber width is 50 micrometers and the approximate average fiber width is 30 micrometers. Also, it is stated that CEPO SS/200 cellulose has an approximate maximum fiber length of 150 micrometers, an approximate average fiber length of 50 micrometers, an approximate maximum fiber width of 45 micrometers and an approximate average fiber width of 25 micrometers. Cellulose fibers with these dimensions are very well suited for the purpose of the invention.

The binders used in the process are the binders conventionally used in the field of granulation with a high melting point or with no melting point at all and of a nonwaxy nature, e.g., polyvinyl pyrrolidone, dextrine, polyvinylalcohol, and cellulose derivatives, including for example hydroxypropyl cellulose, methyl cellulose or CMC. A granulate cannot be formed on the basis of cellulose, filler, enzyme, alkaline buffer salt material and a binder, without the use of a granulating agent, as defined below.

The term "enzyme" as used herein means raw enzyme unless otherwise specified. The term "enzyme powder" means raw enzyme mixed with inorganic salts such as NaCl and, $CaCl_2$. All enzymes can be granulated by means of said process. Preferably, amylases and proteinases are granulated according to the invention. Specific examples are ALCALASE® a Bacillus licheniformis proteinase), ESPERASE® and SAVINASE® (microbial alcaline proteinases produced according to British Pat. No. 1,243,784) and TERMAMYL®(a Bacillus licheniformis amylase). The enzyme can be introduced into the granulator as a precried milled powder or as a solution, for example, a concentrated enzyme solution prepared by ultrafiltration, reverse osmosis or evaporation.

The granulating agent is water and/or a waxy substance. The granulating agent is always used as a liquid phase in the granulation process; the waxy substance if present therefore is either dissolved or dispersed in the water or melted. By a "waxy substance" is understood a "wax" which possesses all of the following characteristics: (1) the melting point is between 30° and 100°C, preferably between 40° and 60°C, (2) the substance is of a tough and not brittle nature, and (3) the substance possesses substantial plasticity at room temperature.

Both water and waxy substance are granulating agents, i.e., they are both active during the formation of the granulate; the waxy substance stays as a constituent in the finished granulate, whereas the majority of the water is removed during the drying. Thus, in order to refer all amounts to the finished, dry granulate, all percentages are calculated on the basis of total dry granulate unless otherwise specified, which means that water, one of the granulating agents, is not added to the other constituents when calculating the percentage of water, whereas the waxy substance, the other granulating agent, has to be added to the other dry constituents when calculating the percentage of waxy substance. Examples of waxy substances are polyglycols, fatty alcohols, ethoxylated fatty alcohols, higher fatty acids, mono-, di- and triglycerolesters of higher fatty acids, e.g., glycerol monostearate, alkylarylethoxylates, and coconut monoethanolamide.

An illustrative summary of a process used to make an enzyme granulate is:

1. Provide dry enzyme powder, cellulose fillers, alkaline buffer salt materials and binders.
2. Mix the dry powders of the granulate.
3. Wet the powder mixture with granulating agent, e.g., water or waxy melt.

4. Process the wet powder mixture of Step 3 in a granulating apparatus (rotating knife) until the granulate has the desired particle size distribution.

A cylindrical Lodige type mixer FM 130 DIZ (U.S. Pat. No. 3,027,102) can be used in the process for this step. The mixer is equipped with both plough shaped mixers mounted on a horizontal (axial) rotating shaft and a granulating device, consisting of one or more cross knives mounted on a shaft introduced into the mixer through the cylindrical wall in a direction perpendicular to the abovementioned horizontal rotating shaft (i.e., radial of the cylinder).

5. Dry in a fluidized bed the moist granulate of Step 4 until a dryness which satisfies both the requirements of enzyme stability and the requirements of free-flowing properties and mechanical strength. Usually this will correspond to a water content less than 10%, preferably less than 3% and more preferably bone dry. In the instances where the granulating agent is exclusively or principally a waxy substance only cooling may be required.

6. Optionally coating the enzyme granulate with an alkaline buffer salt coating, a waxy or some other compatible substance.

Optional Alkaline Buffer Salt Coating of the Enzyme Granulate

The enzyme granulate produced in the present invention can also be coated with alkaline buffer salt using any number of known apparatuses. Coating in a fluidized bed is preferred. Examples of suitable apparatuses and processes are disclosed in U.S. Pat. Nos. 3,196,827, Wurster and Lindlof, issued July 27, 1965; 3,253,944, Wurster, issued May 31, 1966; and 3,117,027, Lindlof and Wurster, issued Jan. 7, 1964.

U.S. Pat. No. 3,117,027 discloses a preferred fluidized bed apparatus which can be used for coating the enzyme granulates produced in the present invention. The fluidized bed will provide substantially uniformly enzyme coated granulates.

The coating process of the present invention comprises e.g.,:

1. Forming an enzyme granulate having a particle size of from 100 to 1600 micrometers, preferably 200 to 800 micrometers, with or without optional waxy coating.

2. Coating the enzyme granulate with an effective amount of alkaline buffer salt material, preferably at a level of from 10% to 100% by weight of the enzyme granulate on a dry weight basis. The enzyme granulate should be surrounded by the coating and the coating should contain an effective amount of alkaline buffer salt.

The protective coating is preferably applied to the enzyme granulate as a 15% to 70% (preferably 20% to 50%) solids aqueous solution in a fluidized bed. The temperature range of the solution can be 60-82° C (140-180° F), and is preferably 65-77° C (150-170° F). The air temperature of the fluidized bed is 45° to 77° C for the coating/drying operation. The rate of addition of the coating solution and the rate of drying are dependent on the solution concentration, temperature of air and volume.

Calcium Present in Granulate and Coating

The enzyme granulate of this invention can be improved if it contains from 40 to 3000 ppm of calcium calculated as calcium chloride. Calcium can be added to the granulate as calcium chloride or calcium sulfate powder in the granulation process or by using water containing a calcium content of 100-500 ppm, preferably 170-300 ppm, calculated as calcium chloride in the water used in the granulation and/or coating process.

Optional Waxy Coating Material

A nonionic waxy material can be applied over the enzyme granulate or over the alkaline buffer salt coated enzyme granulate. The practical levels of optional waxy coating material is up to 57% by weight of the composition, preferably 5-30%. Examples of such waxy coatings are polyethylene glycols, fatty alcohols, ethoxylated fatty alcohols, higher fatty acids, mono-, di- and triglycerolesters of fatty acids, e.g., glycerol monostearate, alkylarylethoxylates and coconut monoethanolamide. Preferred nonionic waxy substances are TAE_{22} (tallow alcohol condensed with 22 moles of ethylene oxide per mole of alcohol), PEG 1500-8000 (polyethylene glycol of molecular weight 1500-8000) and palmitic acid. Other waxy coatings having a melting point of at least 38° C, preferably at least 50° C, can also be used. For example, this waxy coating is melted (50-70° C) and is sprayed onto the granulate in a fluidized bed where cool air (15-30° C) is applied to solidify the waxy coating.

EXAMPLE I

A preferred enzyme granulate can be made using the procedure outlined above using the following ingredients:

Ingredient	Wt%
Proteolytic Enzyme	4
Amylase Enzyme	1
Alkaline Buffer Salt Material[1]	45
Cellulose Filler[2]	20
Binder[3] (polyvinyl pyrrolidone)	5
Waxy Overcoat (PEG 1500)	25

[1] 20% $KHCO_3$, 5% Na_2SO_3, 20% $CaCl_2$/NaCl

[2] Cellulose Powder - CEPO S20

[3] Selected from polyvinyl pyrrolidone, dextrin, polyvinyl alcohols and cellulose derivatives.

EXAMPLE II

A 6 inch Wurster Fluidized Bed Coating Unit with a capacity of about 1 liter can be used. The enzyme granulate of Example I can be optionally coated as follows: 800 grams of enzyme granulate are added to the fluid bed dryer. To this a 1,000 gram 70°C aqueous solution, containing 200 grams of potassium bicarbonate and 40 grams of sodium sulfite, is sprayed on. The coated enzyme granulate is then dried at a fluid bed temperature of 75°C to contain less than 0.5% water. The coated enzyme granulate is then removed from the fluid bed dryer and weighed to confirm coating level.

About 800 grams of the alkaline buffer salt/antioxidant salt-coated enzyme granulate is then placed back into the fluid bed dryer. To this 200 grams of TAE_{22} are sprayed on at 55°C and allowed to cool in the dryer with air temperature 20°C.

Final weight %:		
Enzyme Granulate		61.54%
Protective Coating:		
Potassium Bicarbonate	15.38	18.46
Sodium Sulfite	3.08	
TAE_{22} Overcoating		20.00
	Total	100.00%

The ratio of enzyme granulate to protective coating is about 3.3 to 1. The pH of the coating is 8.5.

EXAMPLE III

The enzyme granulates similar to that described in Examples I or II are dry mixed with peroxyacid bleach granulates.

	Wt%		Grams
Peroxyacid Bleach Granulate			
Diperoxydo-decanedioic Acid	20.75		
Dodecanedioic Acid	1.85		
Boric Acid	22.75		
Na_2SO_4	28.06		
Sodium Acid Pyrophosphate	5.00		
C_{13}LAS	4.50		
		83	20
Enzyme Granulate of Example I or II*		17	4
		100	24

*2.0 Au/gram protease activity.

The process used to make the peroxyacid bleach granulate in Example III is disclosed in U.S. Pat. No. 4,497,757, Beimesch and Hortel, issued Feb. 2, 1985.

EXAMPLE IV

A detergent powder containing the following components:

	Weight %
Diperoxydodecanedioic acid bleach granulate (Ex. III)	25
Enzyme granulates of Example I or II	2
Sodium salt of straight chain C_{12} alkylbenzene sulfonate	20
Sodium tripolyphosphate	35
Sodium sulfate	12
Sodium silicate	4
Brightener	1
Perfume capsules	0.3
Water, perfume	Balance

EXAMPLE V

A laundry additive containing the following components:

	Weight %
Diperoxydodecanedioic acid bleach granulate*	90.2
Enzyme granulates of Example I or II	2
Brightener and sodium silicate	7
Perfume capsules	0.3
Water	Balance

*The peroxyacid bleach granulate of Example III is cut with sodium sulfate to adjust peroxyacid level to about 8% of the bleach granulate.

This invention offers an improved storage stable granular composition comprising an enzyme granulate which is storage stable with a peroxyacid bleach granulate, enabling them to be used together in a detergent or laundry additive product for combined bleaching and stain removal performance.

Claims

1. A storage stable granular composition comprising:
(I) an enzyme granulate including a homogeneous mixture of 0.5% to 20% raw enzyme, 3% to 97.5% alkaline buffer salt material, 2% to 40% cellulosic filler and binder, with said enzyme having an activity of 0.25-10 Au/gram, and
(II) a peroxyacid bleach granulate,
wherein said (I) and (II) have a weight ratio of from 1:1 to 1:1500;
wherein said alkaline buffer salt material has a pH of from 7 to 11, measured as a 10% solution;
wherein said raw enzyme and said alkaline buffer salt material have a weight ratio of from 1:4 to 1:200;
wherein said cellulosic filler and binder of said (I) have a weight ratio of 1:1 to 10:1.

2. The granular composition of Claim 1 wherein said alkaline buffer salt material is selected from the group consisting of potassium bicarbonate, potassium carbonate, tetrapotassium pyrophosphate, tripotassium polyphosphate, sodium bicarbonate and sodium carbonate, preferably potassium bicarbonate.

3. The granular composition of Claim 1 wherein said alkaline buffer salt material includes an antioxidant inorganic salt selected from the group consisting of sodium sulfite, sodium bisulfite and sodium thiosulfate, and mixtures thereof, wherein said antioxidant to alkaline buffer salt have a weight ratio of from 10:1 to 1:50.

4. The granular composition of Claim 1, 2 or 3 wherein said (I) and said (II) have a weight ratio of 1:3 to 1:30 and said pH is 8 to 10 and said raw enzyme and said alkaline buffer salt material have a weight ratio of 1:6 to 1:100.

5. The granular composition of Claim 1, 2 or 3 wherein said raw enzyme and said alkaline buffer salt material have a weight ratio of 1:20 to 1:50.

6. The granular composition of Claim 1, 2 or 3 wherein said enzyme granulate is coated with a protective coating containing an effective amount of alkaline buffer salt material having a pH of from 7 to 11; said protective coating surrounding said enzyme granulate and providing improved enzyme stability in the presence of said peroxyacid bleach granulate.

7. The granular composition of Claim 6 wherein said protective coating is from 10% to 67% by weight of

said coated enzyme granulate.

8. The granular composition of Claim 6 wherein said protective coating surrounding said enzyme granulate is from 50% to 80% by weight of said coated enzyme granulate.

9. The granular composition of Claim 6 wherein said protective coating contains 50% to 100% alkaline buffer salt by weight of said protective coating.

10. The granular composition of Claims 6 wherein said protective coating contains 50-100% alkaline buffer salt by weight of said protective coating, and wherein said alkaline buffer salt is present at a level of from 5% to 10% by weight of said enzyme granulate, and wherein the balance of said protective coating is selected from antioxidants, calcium chloride and other compatible inorganic salts.

11. The granular composition of Claim 6 wherein said alkaline buffer salt material protective coating has a pH of 8-10, said enzyme granulate and said protective coating having a ratio of from 4:1 to 1:1.

12. The granular composition of Claim 1, 2 or 3 wherein antioxidant is present at a level of 1% to 40% by weight of said enzyme granulate and said alkaline buffer salt is present at an effective level to stabilize said enzyme from rapid deactivation in the presence of peroxyacid bleach granulate.

13. The granular composition of Claim 12 wherein said antioxidant is present at a level of 2% to 30% by weight of said enzyme granulate.

14. The granular composition of Claim 6 wherein said protective coating is a mixture of alkaline buffer salt and antioxidant, said coating having a pH of 8 to 10.

15. The granular composition of Claim 6 wherein said alkaline buffer salt is selected from the group consisting of potassium bicarbonate, potassium carbonate, tetrapotassium pyrophosphate, tripotassium polyphosphate, sodium bicarbonate and sodium carbonate, and mixtures thereof, said alkaline buffer salt in said protective coating being present at a level of 5% to 50% by weight of said enzyme granulate.

16. The granular composition of Claim 1, 2 or 3 wherein said enzyme granulate contains calcium ion derived from calcium sulfate or calcium chloride at a level of 40 to 3000 ppm by weight of said enzyme granulate, calculated as calcium chloride.

17. The granular composition of Claim 1, 2 or 3 wherein said enzyme granulate is surrounded with a coating of water-soluble nonionic wax having a melting point of at least 38 °C.

18. The granular composition of Claim 1, 2 or 3 wherein said enzyme granulate includes a nonionic waxy coating at a level of from 5% to 57% by weight of said enzyme granulate, and has a melting point of at least 50 °C.

19. The granular composition of Claim 18 wherein said coating of said water-soluble nonionic waxy coating is present at a level of 10% to 30% by weight of said enzyme granulate.

20. The granular composition of Claim 18 wherein said water-soluble nonionic waxy coating is present at a level of 15% to 25% by weight of said enzyme granulate.

21. The granular composition of Claim 17 wherein said nonionic wax is selected from the group consisting of: fatty alcohols, ethoxylated fatty alcohols, higher fatty acids, mono-, di- and triglycerolesters of fatty acids, e.g., glycerol monostearate, alkylarylethoxylates and coconut monoethanolamide, and mixtures thereof.

22. The granular composition of Claim 21 wherein said nonionic wax is selected from the group consisting of: TAE_{25}, PEG 1500-8000 and palmitic acids.

23. The granular composition of any of the previous claims characterized in that said homogenous mixture

of raw enzyme is a homogenous mixture of proteolytic and amylolytic enzymes.

Revendications

1. Composition granulaire stable au stockage, comprenant :
(i) un granulé contenant une enzyme, comprenant un mélange homogène de 0,5 à 20 % d'une enzyme brute, 3 à 97,5 % d'un sel tampon alcalin, 2 à 40 % d'une charge cellulosique et d'un liant, cette enzyme ayant une activité de 0,25-10 Au/g et
(ii) un granulé contenant un agent de blanchiment aux peracides,
les granulés (i) et (ii) étant présents selon une proportion pondérale de 1:1 à 1:1500 ;
où ledit sel tampon alcalin a un pH de 7 à 11, mesuré en solution à 10 % ;
où ladite enzyme brute et ledit sel tampon alcalin sont présents selon une proportion pondérale de 1:4 à 1:200 ;
où ladite charge cellulosique et ledit liant dudit granulé (i) sont présents en une proportion pondérale de 1:1 à 10:1.

2. Composition granulaire selon la revendication 1, dans laquelle ledit sel tampon alcalin est choisi dans le groupe comprenant le bicarbonate de potassium, le carbonate de potassium, le pyrophosphate tétrapotassique, le polyphosphate tripotassique, le bicarbonate de sodium et le carbonate de sodium, de préférence le bicarbonate de potassium.

3. Composition granulaire selon la revendication 1, dans laquelle ledit sel tampon alcalin comprend un sel minéral anti-oxydant choisi dans le groupe comprenant le sulfite de sodium, le bisulfite de sodium et le thiosulfate de sodium et leurs mélanges, la proportion pondérale dudit anti-oxydant au sel tampon alcalin étant de 10:1 à 1:50.

4. Composition granulaire selon la revendication 1, 2 ou 3, dans laquelle la proportion pondérale dudit granulé (i) audit granulé (ii) est de 1:3 à 1:30, et ledit pH est de 8 à 10, et la proportion pondérale de ladite enzyme brute audit sel tampon alcalin est de 1:6 à 1:100.

5. Composition granulaire selon la revendication 1, 2 ou 3, dans laquelle la proportion pondérale de ladite enzyme brute audit sel tampon alcalin est de 1:20 à 1:50.

6. Composition granulaire selon la revendication 1, 2 ou 3, dans laquelle ledit granulé contenant une enzyme est enrobé d'un enrobage protecteur contenant une quantité efficace d'un sel tampon alcalin ayant un pH de 7 à 11 ; ledit enrobage protecteur entourant ledit granulé contenant une enzyme et conférant une meilleure stabilité de l'enzyme en présence dudit granulé contenant un agent de blanchiment aux peracides.

7. Composition granulaire selon la revendication 6, dans laquelle ledit enrobage protecteur est présent en une quantité de 10 à 67 % en poids par rapport audit granulé contenant une enzyme enrobée.

8. Composition granulaire selon la revendication 6, dans laquelle ledit enrobage protecteur qui entoure ledit granulé contenant l'enzyme est présent en une quantité de 5 à 60 % en poids par rapport audit granulé contenant une enzyme enrobée.

9. Composition granulaire selon la revendication 6, dans laquelle ledit enrobage protecteur contient 50 à 100 % en poids du sel tampon alcalin par rapport audit enrobage protecteur.

10. Composition granulaire selon la revendication 6, dans laquelle ledit enrobage protecteur contient 50 à 100 % en poids du sel tampon alcalin par rapport audit enrobage protecteur, et dans laquelle ledit sel tampon alcalin est présent en une quantité de 5 à 10 % en poids par rapport audit granulé contenant une enzyme, et dans laquelle le reste dudit enrobage protecteur est choisi parmi les anti-oxydants, le chlorure de calcium et d'autres sels minéraux compatibles.

11. Composition granulaire selon la revendication 6, dans laquelle ledit enrobage protecteur contenant un sel tampon alcalin a un pH de 8 à 10, la proportion dudit granulé contenant une enzyme et dudit enrobage protecteur étant de 4:1 à 1:1.

12. Composition granulaire selon la revendication 1, 2 ou 3, dans laquelle l'anti-oxydant est présent en une quantité de 1 à 40 % en poids par rapport audit granulé contenant une enzyme, ledit sel tampon alcalin étant présent en une quantité efficace permettant de stabiliser ladite enzyme contre une rapide désactivation en présence d'un granulé contenant un agent de blanchiment aux peracides.

13. Composition granulaire selon la revendication 12, dans laquelle ledit anti-oxydant est présent en une quantité de 2 à 30 % en poids par rapport audit granulé contenant une enzyme.

14. Composition granulaire selon la revendication 6, dans laquelle ledit enrobage protecteur est un mélange du sel tampon alcalin et d'un anti-oxydant, cet enrobage ayant un pH de 8 à 10.

15. Composition granulaire selon la revendication 6, dans laquelle ledit sel tampon alcalin est choisi dans le groupe comprenant le bicarbonate de potassium, le carbonate de potassium, le pyrophosphate tétrapotassique, le polyphosphate tripotassique,le bicarbonate de sodium et le carbonate de sodium et leurs mélanges, ledit sel tampon alcalin dudit enrobage protecteur étant présent en une quantité de 5 à 50 % en poids par rapport audit granulé contenant une enzyme.

16. Composition granulaire selon la revendication 1, 2 ou 3, dans laquelle ledit granulé contenant une enzyme contient un ion calcium dérivant du sulfate de calcium ou du chlorure de calcium en une quantité de 40 à 3000 ppm en poids par rapport audit granulé contenant une enzyme, cette quantité étant calculée sous forme de chlorure de calcium.

17. Composition granulaire selon la revendication 1, 2 ou 3, dans laquelle ledit granulé contenant une enzyme est entouré d'un enrobage constitué d'une cire non-ionique soluble dans l'eau ayant un point de fusion d'au moins 38 °C.

18. Composition granulaire selon la revendication 1, 2 ou 3, dans laquelle ledit granulé contenant une enzyme comprend un enrobage du type cire non ionique, en une quantité de 5 à 57 % en poids par rapport audit granulé contenant une enzyme, et a un point de fusion d'au moins 50 °C.

19. Composition granulaire selon la revendication 18, dans laquelle ledit enrobage constitué d'une cire non ionique soluble dans l'eau est présent en une quantité de 10 à 30 % en poids par rapport audit granulé contenant une enzyme.

20. Composition granulaire selon la revendication 18, dans laquelle ledit revêtement du type cire non ionique soluble dans l'eau est présent en une quantité de 15 à 25 % en poids par rapport audit granulé contenant une enzyme.

21. Composition granulaire selon la revendication 17, dans laquelle ladite cire non ionique est choisie dans le groupe comprenant les alcools gras, les alcools gras éthoxylés, les acides gras supérieurs, les esters du mono-, du di-et du triglycérol d'acides gras, par exemple le monostéarate de glycérol, les dérivés alkylaryliques polyéthoxylés et le (huile de coprah)-monoéthanolamide, et leurs mélanges.

22. Composition granulaire selon la revendication 21, dans laquelle ladite cire non ionique est choisie dans le groupe comprenant le TAE_{22}, le PEG 1500-8000 et les acides palmitiques.

23. Composition granulaire selon l'une quelconque des revendications précédentes, caractérisée en ce que ledit mélange homogène de l'enzyme brute est un mélange homogène d'enzymes protéolytiques et d'enzymes amylolytiques.

Patentansprüche

1. Eine lagerstabile granulierte Zusammensetzung, enthaltend:
   (I) ein Enzymgranulat, umfassend eine homogene Mischung aus 0,5 bis 20 % Rohenzym, 3 bis 97,5 % eines alkalischen Puffersalzmaterials, 2 bis 40 % eines Cellulose-Füllmaterials und eines Bindemittels, wobei das Enzym eine Aktivität von 0,25 bis 10 Au/g aufweist, und
   (II) ein Peroxysäure-Bleichmittelgranulat,
   worin das Gewichtsverhältnis von (I) und (II) 1:1 bis 1:1500 beträgt:

das alkalische Puffersalzmaterial einen pH-Wert von 7 bis 11, als 10%ige Lösung gemessen, hat; worin das rohe Enzym und das alkalische Puffersalzmaterial ein Gewichtsverhältnis von 1:4 bis 1:200 aufweisen; und worin das Cellulose-Füllmaterial und das Bindemittel gemäß (I) ein Gewichtsverhältnis von 1:1 bis 10:1 aufweisen.

2. Granulierte Zusammensetzung gemäß Anspruch 1, worin das alkalische Puffersalzmaterial ausgewählt ist aus der Gruppe bestehend aus Kaliumbicarbonat, Kaliumcarbonat, Tetrakaliumpyrophosphat, Trikaliumpolyphosphat, Natriumbicarbonat und Natriumcarbonat, vorzugsweise Kaliumbicarbonat.

3. Granulierte Zusammensetzung gemäß Anspruch 1, worin das alkalische Puffersalzmaterial ein Antioxidans in Form eines anorganischen Salzes umfaßt, welches ausgewählt ist aus der Gruppe bestehend aus Natriumsulfit, Natriumbisulfit und Natriumthiosulfat sowie deren Mischungen, wobei das Gewichtsverhältnis von Antioxidans zu alkalischem Puffersalz 10:1 bis 1:50 beträgt.

4. Granulierte Zusammensetzung gemäß Anspruch 1, 2 oder 3, worin das Gewichtsverhältnis von (I) und (II) 1:3 bis 1:30, der pH-Wert 8 bis 10 und das Gewichtsverhältnis von rohem Enzym und alkalischem Puffersalzmaterial 1:6 bis 1:100 beträgt.

5. Granulierte Zusammensetzung gemäß Anspruch 1, 2 oder 3, worin das Gewichtsverhältnis von rohem Enzym und alkalischem Puffersalzmaterial 1:20 bis 1:50 beträgt.

6. Granulierte Zusammensetzung gemäß Anspruch 1, 2 oder 3, worin das Enzymgranulat mit einem Schutzüberzug versehen ist, welcher eine wirksame Menge eines alkalischen Puffersalzmaterials mit einem pH-Wert von 7 bis 11 enthält, wobei dieser Schutzüberzug das Enzymgranulat umgibt und zu einer verbesserten Stabilität des Enzyms in Gegenwart des Peroxysäure-Bleichmittelgranulats führt.

7. Granulierte Zusammensetzung gemäß Anspruch 6, worin der Schutzüberzug 10 bis 67 Gew.-%, bezogen auf das überzogene Enzymgranulat, ausmacht.

8. Granulierte Zusammensetzung gemäß Anspruch 6, worin dieser, das Enzymgranulat umgebende Schutzüberzug 50 bis 80 Gew.-% des überzogenen Enzymgranulats ausmacht.

9. Granulierte Zusammensetzung gemäß Anspruch 6, worin der Schutzüberzug 50 bis 100 Gew.-% alkalisches Puffersalz, bezogen auf den Schutzüberzug, enthält.

10. Granulierte Zusammensetzung gemäß Anspruch 6, worin der Schutzüberzug 50 bis 100 Gew.-% alkalisches Puffersalz, bezogen auf den Schutzüberzug, enthält und das alkalische Puffersalz in einer Menge von 5 bis 10 Gew.-%, bezogen auf das Enzymgranulat, vorhanden ist und der Rest des Schutzüberzugs ausgewählt ist aus Antioxidantien, Calciumchlorid und anderen kompatiblen anorganischen Salzen.

11. Granulierte Zusammensetzung gemäß Anspruch 6, worin der Schutzüberzug mit dem alkalischen Puffersalzmaterial einen pH-Wert von 8 bis 10 aufweist und das Gewichtsverhältnis von Enzymgranulat zu Schutzüberzug 4:1 bis 1:1 beträgt.

12. Granulierte Zusammensetzung gemäß Anspruch 1, 2 oder 3, worin das Antioxidans in einer Menge von 1 bis 40 Gew.-%, bezogen auf das Enzymgranulat, vorhanden ist und das alkalische Puffersalz in einer wirksamen Menge vorhanden ist, um das Enzym hinsichtlich einer raschen Desaktivierung in Gegenwart des Peroxysäure-Bleichmittelgranulats zu stabilisieren.

13. Granulierte Zusammensetzung gemäß Anspruch 12, worin das Antioxidans in einer Menge von 2 bis 30 Gew.-%, bezogen auf das Enzymgranulat, vorhanden ist.

14. Granulierte Zusammensetzung gemäß Anspruch 6, worin der Schutzüberzug eine Mischung aus dem alkalischen Puffersalz und dem Antioxidans ist und der Überzug einen pH-Wert von 8 bis 10 aufweist.

15. Granulierte Zusammensetzung gemäß Anspruch 6, worin das alkalische Puffersalz ausgewählt ist aus

der Gruppe bestehend aus Kaliumbicarbonat, Kaliumcarbonat, Tetrakaliumpyrophosphat, Trikaliumpolyphosphat, Natriumbicarbonat und Natriumcarbonat sowie deren Mischungen und worin das alkalische Puffersalz im Schutzüberzug in einer Menge von 5 bis 50 Gew.-%, bezogen auf das Enzymgranulat, vorhanden ist.

16. Granulierte Zusammensetzung gemäß Anspruch 1, 2 oder 3, worin das Enzymgranulat Calciumionen, erhalten aus Calciumsulfat oder Calciumchlorid, in einer Menge von 40 bis 3000 ppm, bezogen auf das Gewicht des Enzymgranulats und berechnet als Calciumchlorid, enthält.

17. Granulierte Zusammensetzung gemäß Anspruch 1, 2 oder 3, worin das Enzymgranulat mit einem Überzug aus einem wasserlöslichen nichtionischen Wachs mit einem Schmelzpunkt von wenigstens 38 °C umgeben ist.

18. Granulierte Zusammensetzung gemäß Anspruch 1, 2 oder 3, worin das Enzymgranulat einen nichtionischen Wachsüberzug in einer Menge von 5 bis 57 Gew.-%, bezogen auf das Enzymgranulat, mit einem Schmelzpunkt von wenigstens 50 °C umfaßt.

19. Granulierte Zusammensetzung gemäß Anspruch 18, worin der Überzug aus dem wasserlöslichen nichtionischen Wachs in einer Menge von 10 bis 30 Gew.-%, bezogen auf das Enzymgranulat, vorhanden ist.

20. Granulierte Zusammensetzung gemäß Anspruch 18, worin der wasserlösliche nichtionische Wachsüberzug in einer Menge von 15 bis 25 Gew.-%, bezogen auf das Enzymgranulat, vorhanden ist.

21. Granulierte Zusammensetzung gemäß Anspruch 17, worin das nichtionische Wachs ausgewählt ist aus der Gruppe bestehend aus: Fettalkoholen, ethoxylierten Fettalkoholen, höheren Fettsäuren, Mono-, Di- und Triglyceroiestern von Fettsäuren, z.B. Glycerolmonostearat, Alkylarylethoxylaten und Kokosnußmonoethanolamid, sowie deren Mischungen.

22. Granulierte Zusammensetzung gemäß Anspruch 21, worin das nichtionische Wachs ausgewählt ist aus der Gruppe bestehend aus: TAE_{22}, PEG 1500-8000 und Palmitinsäuren.

23. Granulierte Zusammensetzung gemäß einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß die homogene Mischung des Rohenzyms eine homogene Mischung aus proteolytischen und amylolytischen Enzymen ist.